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PHENYLENE SULFIDE POLYMERS

TECHNICAL DOCUMENTARY REPORT NO. ASD-TDR-62-322
March 1962

Directorate Of Materials And Processes
Aeronautical Systems Division
Air Force Systems Command
Wright-Patterson Air Force Base, Ohio

Project No. 7340, Task No. 734004

(Prepared under Contract No. AF 33(616)-7251
by The Dow Chemical Company, Midland, Michigan;
Harry A. Smith and Carl E. Handlovits, authors)

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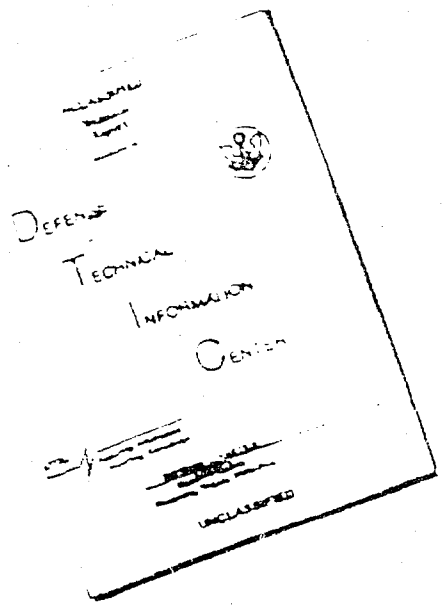

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FOREWORD

This report was prepared by The Dow Chemical Company under USAF Contract No. AF 33(616)-7251. This contract was initiated under Project No. 7340, "Non-metallic and Composite Materials", Task No. 73404, "New Chemicals and Methods." The work was administered under the direction of Directorate of Materials and Processes, Aeronautical Systems Division, with Mr. G. A. Loughran acting as project engineer.

This report covers work conducted from April 1961 to February 1962.

This report was prepared by Dr. Harry A. Smith, Project Director. The laboratory work was conducted by Drs. Robert W. Lenz and Harry A. Smith, Carl E. Handlovits, William K. Carrington and James B. Louch. The administrator of the contract is Dr. W. R. Nummy, Director of the Polymer Research Laboratory.

ABSTRACT

The investigation of phenylene sulfide polymers has been divided into four areas of endeavor. These are a kinetic study of a model reaction, monomer synthesis, polymerization, and determination of polymer properties. From the results of the kinetic study and monomer synthesis coupled with the early results in the other two fields cuprous p-bromothiophenoxide has been chosen as the monomer of choice for the preparation of linear phenylene sulfide polymers. Later work on this monomer has shown that a number average degree of polymerization greater than 400 can be obtained either by solid state or solution polymerization. This polymer which has useful polymeric properties is stable in air or nitrogen to 450°C and forms a polymeric residue stable to 900°C under nitrogen.

PUBLICATION REVIEW

This report has been reviewed and is approved.

FOR THE COMMANDER:

William E. Gibbs

WILLIAM E. GIBBS
Acting Chief, Polymer Branch
Nonmetallic Materials Laboratory
Directorate of Materials and Processes

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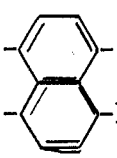
VIII.	Polymerization of NaS-  -F	22
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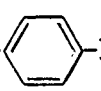
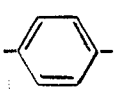
X.	Solution Polymerization of KS-  -Br	24
XI.	Polymerization of (p)X-  -SM	26
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I. INTRODUCTION

The purpose of this work is to obtain a useful plastic material which is thermally stable. The initial work on phenylene sulfide polymers was done by Dr. A. D. Macallum of London, Ontario. He discovered that this polymer could be prepared by the sequence of reactions shown in Figure 1.

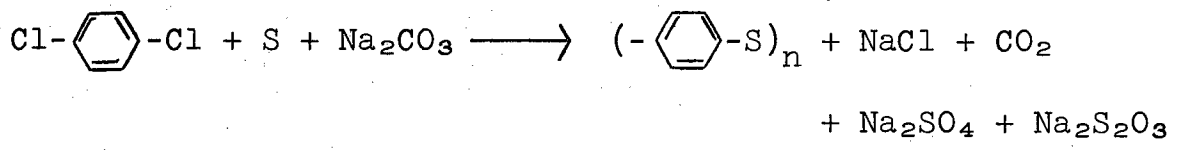

Figure 1. Macallum Polymerization

Since Dow makes p-dichlorobenzene and the other two starting materials are inexpensive, the patents for this work were purchased from Dr. Macallum by The Dow Chemical Company in 1954. Subsequent studies were carried on in the Plastics Department Research Laboratories.

It soon became apparent that the Macallum polymerization would be a difficult reaction to control since the yields and the polymer properties were very unpredictable. In addition the polymeric material obtained was somewaht branched and or lightly crosslinked, and also there was always found an insoluble, infusible highly crosslinked material. Consequently, it was decided to prepare a more readily characterizable polymer namely a linear polymer from the condensation polymerization of such species as p-halothiophenoxides.

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II. RESULTS AND DISCUSSION

In the course of the investigation on linear phenylene sulfide polymers five different aspects of the problem were studied. These were (1) a kinetic study of the polymerization on model compounds, (2) monomer synthesis, (3) polymerization studies, (4) determination of the polymer properties, and (5) crosslinking studies.

Kinetic Studies

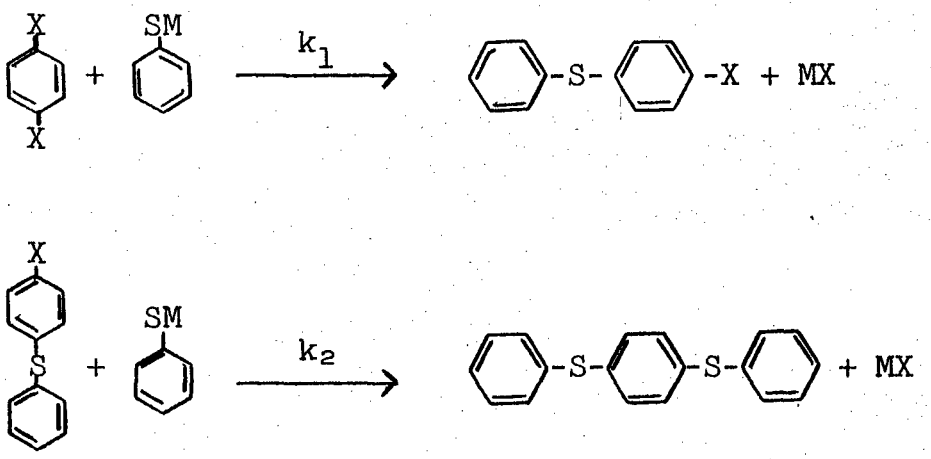
The first phase of our work was to study the basic polymerization reactions. Since isolation of individual products from a polymerization reaction would be at best difficult, it was decided to investigate a model reaction. From this it was hoped to determine the relative reactivities of the various halogens and cations used as well as the side reactions involved in the use of each halogen and cation. Having this information then, a monomer system could be chosen which would have the greatest possibility of producing a high molecular weight polymer by condensation polymerization.

The system studied is depicted in Figure 2. As can be seen, the reaction takes place in two steps. In the first step p-dihalobenzene and thiophenoxide react to give p-halophenyl phenyl sulfide. This then reacts with more thiophenoxide in the second step to give 1,4-bis(phenylthio)benzene.

For the kinetic consideration of the reaction, it was treated as a competitive, consecutive second order reaction. Due to the nature of this type of kinetic treatment the individual rate constants are extremely difficult to determine accurately. However, thanks to Dr. Turner Alfrey, Jr. who worked out the mathematical treatment we were able to obtain quite easily the ratio of the rate constants. This ratio then makes it possible to determine whether a halogen opposite a sulfide linkage (k_2) is more reactive than one opposite the same halogen (k_1). It should be mentioned that when the two halogens have the same reactivity, the ratio of k_2/k_1 equals 0.5.

The starting materials for this study needed to be very pure since by-products were going to be studied also. Consequently the commercial p-dihalobenzenes were recrystallized and then checked for purity by gas-liquid chromatography prior to use. The thiophenoxide after purification was checked for purity by potentiometric titration with silver nitrate. Both reagents had a purity of greater than 99%.

All the reaction and workup procedures were standardized to avoid introducing errors from this source. The reactions were run in sealed glass ampoules under an argon atmosphere. The ampoules were placed in steel jackets and preheated in a molten salt bath



X = F, Cl, Br, I
M = Na, Li, K, Cu

Figure 2. MODEL REACTION FOR KINETIC STUDIES

at 500°C for one minute and forty seconds. Then they were placed in the preheated bomb rocker and allowed to react for the desired time. Zero time for reactions carried out at 250°C was taken as four minutes after the introduction of the bomb into the molten salt bath since calibration runs had indicated that this was the time required for the bomb to reach the reaction temperature. For reaction times of greater than six hours preheat treatment was felt to be unnecessary.

After the reaction was completed, the ampoules were frozen in liquid nitrogen and opened. The contents were extracted with carbon disulfide and then with water. The water extract was titrated with silver nitrate to determine the amount of halide ion liberated. The carbon disulfide extract was analyzed on a model 300 F&M high temperature, linear programmed gas-liquid chromatograph. A sample chromatogram is shown in Figure 3. This figure shows the separation of the products obtained in a typical reaction mixture and their order of elution. Durene, peak 4, is an internal standard. Peaks 8 and 9 are the products of the first and second reactions, respectively (Figure 2). An example of the results from a typical analysis is shown in Table I. As can be seen the results are quite good giving essentially a complete material balance. On the average, however, the results fall in a range of $\pm$ 5% of the values given in Table I.

Two of the products listed in Table I, diphenyl sulfide and diphenyl disulfide, occur in rather small amounts. These are the major by-products in the reaction and amount to 0.2-0.4% of the total products in a solution reaction and 0.2-0.7% in a reaction without solvent. The diphenyl disulfide undoubtedly arises from thiophenoxide being oxidized during the workup. The diphenyl sulfide may arise from disproportionation of the thiophenoxide during the reaction. Other by-products found in only trace quantities are benzene, halobenzene, and free halogen. From the by-product studies it became apparent that in the reaction of sodium thiophenoxide with p-dihalobenzene the order of by-product production for the respective halogens was $I \gg F > Br \sim Cl$.

The order of ease of halogen displacement, however, does not parallel exactly that for by-product production. Some of the kinetic data from the model reactions is shown in Table II. The relative reactivities of the various halogens can be ascertained from the percent dihalobenzene reacted in a given length of time. Seventy-seven percent of the p-difluorobenzene reacted in twelve hours while in the case of the chloro, bromo, and iodo compounds the same extent of reaction is achieved in about five hours, fifteen minutes, and ten minutes respectively as shown by Table II. Therefore the order of reactivity of the dihalobenzenes must be $I > Br > Cl > F$ for the overall reaction.

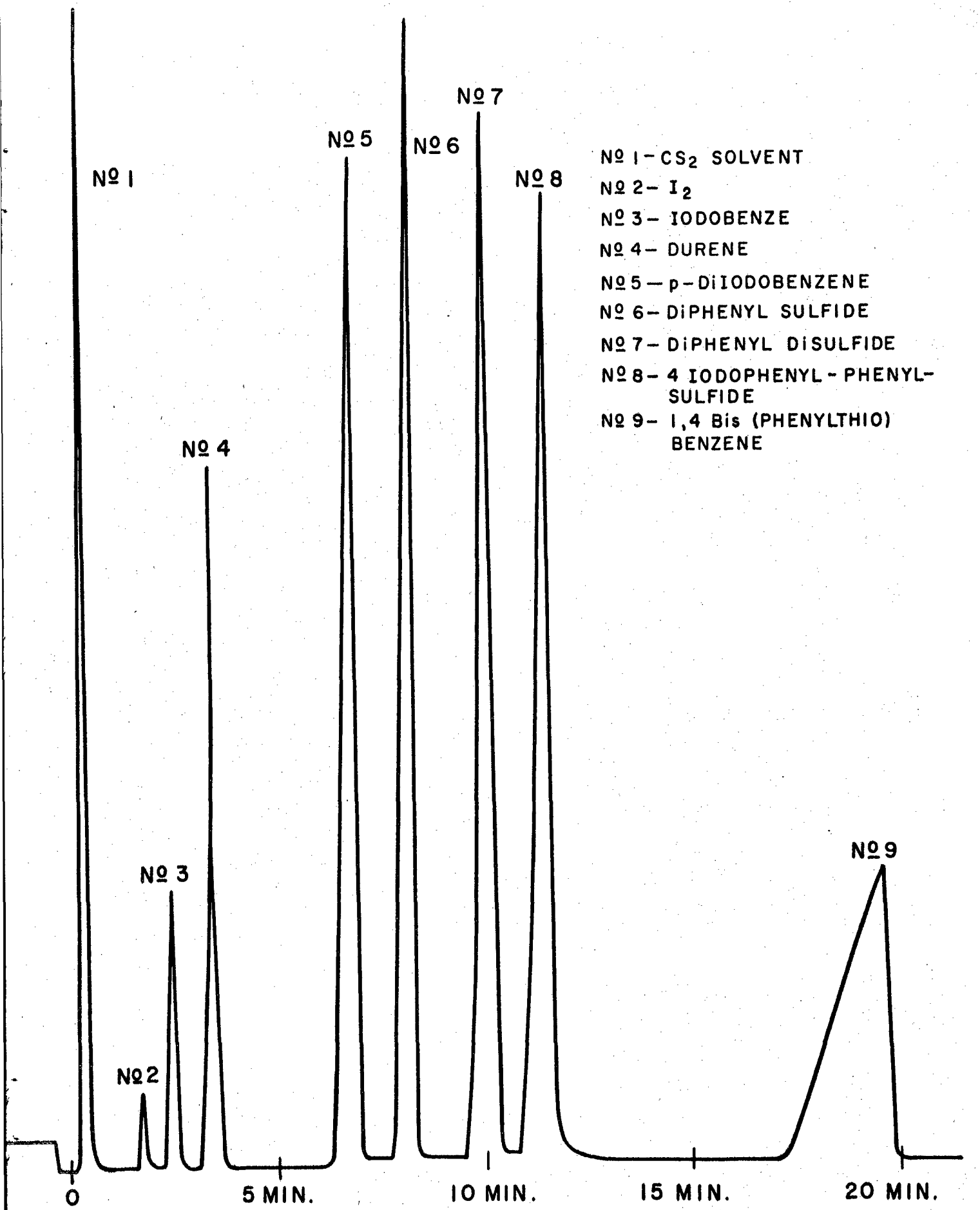


FIGURE 3. MODEL GAS-LIQUID CHROMATOGRAM OF REACTION PRODUCTS

TABLE I

Complete Material Balance of the Reaction of Sodium Thiophenoxide with p-Diiodobenzene

Reactants:	Moles
sodium thiophenoxide	0.0200
p-diiodobenzene	0.0100
Products:	
sodium iodide	0.01635
sodium thiophenoxide	0.00342
p-diiodobenzene	0.00033
p-iodophenyl sulfide	0.00297
p-bis (phenylthio) benzene	0.00660
phenyl sulfide	0.00011
phenyl disulfide	0.00035
Material Balance:	**%**
iodine accounted for	99.9
sulfur accounted for	102.0
benzene accounted for	101.4

TABLE II

Rates of Solution Reactions of
Various p-Dihalobenzenes

p-Dihalobenzene	Time (hrs.)	% X-⬡-X Reacted	k_2k_1	Average
ϕF_2	4.25	50.2	37.9	34.2
	12.0	76.9	30.4	
ϕCl_2	0.25	17.1	1.77	
	0.25	13.4	1.64	1.84
	5.00	70.3	1.98	
	5.00	70.3	1.95	
ϕBr_2	0.25	79.0	0.900	
	0.25	69.9	0.870	0.860
	0.50	83.7	0.804	
ϕI_2	0.18	75.3	0.548	0.543
	0.18	80.0	0.537	

In order to determine the relative reactivities of the respective halogens under the same circumstances in each case and without complications by consecutive, competing reactions, the reaction of p-halophenyl phenyl sulfide with thiophenoxide was studied. The results are given in Table III. It can immediately be seen that the order of replaceability of a halogen opposite a sulfide linkage is I>Br>F~Cl or essentially the same order exhibited in Table II.

Table II also contains some interesting data in the form of k_2/k_1 ratios. These ratios show that an iodine opposite an iodine has about the same reactivity as one opposite a sulfide. (The ratio is about 0.5.) In the case of bromine, however, the bromine opposite a sulfide is 1.5 times more reactive than one opposite a bromine. With chlorine this factor goes to about three times and with fluorine to seventy times. This suggests that in a monomer system containing an aryl fluoride a preferential formation of polymer might be observed. If this happens, it would be possible to obtain high molecular weights at relatively low conversions. Some results in the polymerization studies shed some light on this subject, and it will be discussed further.

It might be mentioned that the k_2's given in Table III should represent the k_2's in the model reaction. Therefore these in conjunction with the k_2/k_1 ratio should allow the k_1's for the model reaction to be calculated.

In addition to the effect on reactivity that the halogen substituent had, it might be expected that the cation associated with the thiophenoxide might show some effect. The results of this study are given in Table IV. From the percent dihalobenzene reacted in a given time it can be seen that the lithium and cuprous salts are both more reactive than the sodium. In addition, since the cuprous salt is reacting with a less reactive halogen and still gives about the same percent reaction as the lithium salt, the cuprous salt must be the more reactive of the two. This gives an order of reactivity of Cu>Li>Na.

The above results coupled with the ease of preparation of the various species, should enable a choice of a monomer to be made. It has been found that the ease of preparation of the thiophenoxides was Cu>Na~K>Li while that for the aryl halide was Br>Cl>F>I. This along with the orders of reactivity and of by-product production indicates that the best choice for monomer would be cuprous p-bromothiophenoxide. In addition, due to the possibilities of preferential formation of polymer, p-fluorothiophenoxide should be considered.

TABLE III

Solution Reactions of
4-Halophenylphenyl Sulfide

Compound	Second Order Rate Constant k_2 (l/mole min.)
FØSØ	0.10 ± 0.02
ClØSØ	0.094
BrØSØ	0.15 ± 0.03
IØSØ	0.65 ± 0.17

TABLE IV

Reactivity of Thiophenoxide Salts with p-Dihalobenzene

Salt	Dihalo-benzene	Time (hrs)	Temp. °C	% X-⟨⟩-X Reacted	k_2/k_1	Average
LiSØ	$ØI_2$	0.25	250	87.5	0.584	0.579
		0.25	250	90.0	0.573	
NaSØ	$ØI_2$	0.25	250	75.3	0.548	0.543
		0.25	250	80.0	0.537	
NaSØ	$ØBr_2$	0.25	250	79.0	0.900	
		0.25	250	69.9	0.870	0.860
		0.50	250	83.7	0.804	
CuSØ	$ØBr_2$	0.17	250	83.9	-	
		1.00	200	80.1	-	
		2.00	200	87.5	-	

Monomer Synthesis

At the same time that the kinetic studies were being carried out, attempts were being made to synthesize all the possible monomer variations. There were three general methods used for the synthesis of the substituted thiophenols desired for the monomers. These are shown in Figure 4. The first involves preparation of the diazonium salt from the appropriate p-haloaniline. This is converted to the xanthate.[1] The xanthate is then pyrolyzed to the desired p-halothiophenol.[1] This technique, however, is long and tedious resulting in a low overall yield of approximately 35-40%. Consequently simpler methods which could give higher yields were desired for the three p-halothiophenols, fluoro, bromo and iodo, which could not be obtained commercially.

It was described in the literature[2] (reaction 2, Figure 4) that treatment of thiophenol with bromine gave the bis-(p-bromophenyl) disulfide in essentially a quantitative yield. This material can be reduced to p-bromothiophenol by zinc-acid reduction (80% yield),[3] by sodium borohydride-aluminum chloride reduction (95-99% yield),[4] or by a sodium hydroxide-dextrose reduction (70% yield).[5]

When an attempt was made to prepare p-iodothiophenol by the same procedure as used for the preparation of bis-(p-bromophenyl) disulfide it was discovered that very little iodo disulfide was formed from iodine and thiophenol. The major product is thianthrene. Consequently a different process was needed, and this is shown in the third reaction and its alternate in Figure 4. Treatment of iodobenzene with sulfur trioxide results in an 81% yield of p-iodobenzenesulfonic acid anhydride monohydrate after seven hours at -60°C.[6] Treatment of the anhydride so formed with hydrobromic acid in acetic acid converts it to the disulfide in a 70% yield.[7] Overall yield to p-iodothiophenol is about 57%. The alternate route, treatment of iodobenzene with chlorosulfonic acid, suffers from a serious side reaction namely the formation of sulfone. Consequently the maximum yield of sulfonyl chloride obtained was 48%. The reduction of the sulfonyl chloride to the disulfide, however, was almost quantitative using hydrobromic acid in acetic acid.[7] This gives an overall yield to p-iodothiophenol of 45%. A point in the favor of the p-iodobenzene sulfonyl chloride route is that the sulfonyl chloride is not converted to an unusable product if it becomes warm as the corresponding sulfonic acid anhydride monohydrate is.

From the substituted thiophenols the salts could be obtained in greater than 95% yield as shown in Figure 5. Reaction (1), the first one tried in an effort to prepare the sodium salts, was successful. Purity and yield, however, frequently suffer due to the environmental instability of the sodium hydride. Consequently a better method of preparing sodium salts in addition to techniques for preparing the other salts was desired.

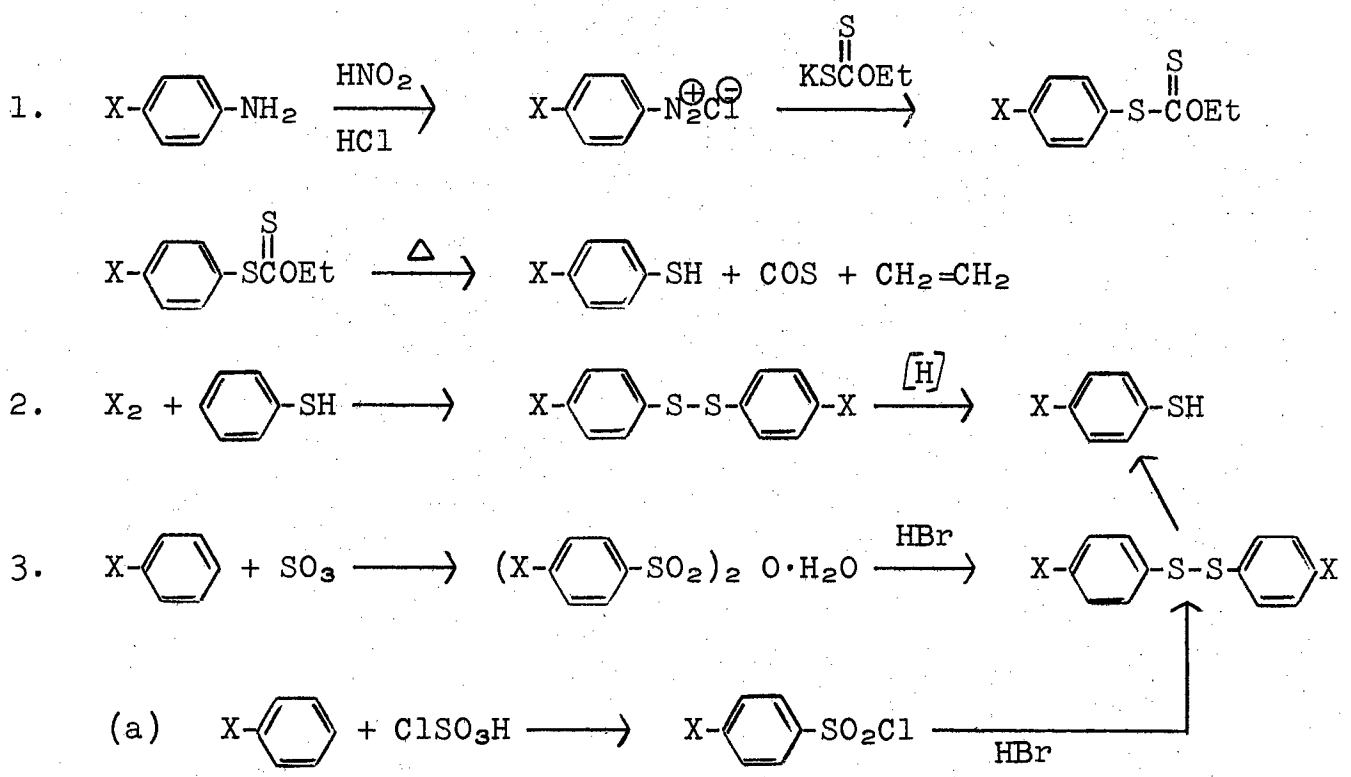
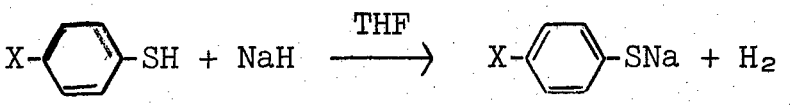
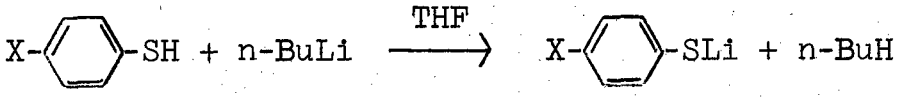
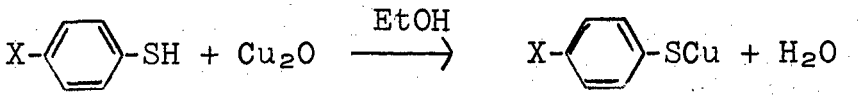
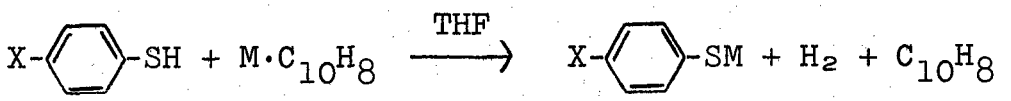


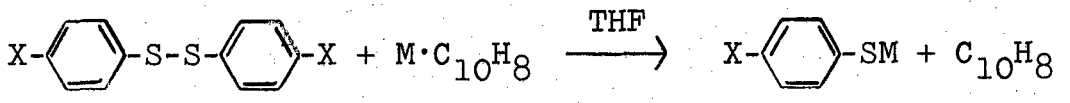
Figure 4. THIOPHENOL SYNTHESIS

1. 

2. 

3. 

4. 

5. 

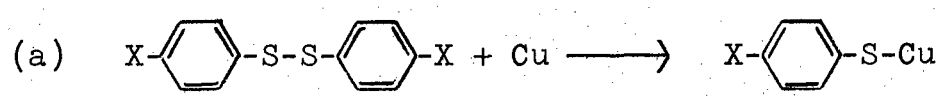
(a) 

Figure 5. SALT PREPARATION

Lithium salts are conveniently prepared by reaction (2) while reaction (3) provides an easy route to the cuprous salts. The cuprous salts provide one distinct advantage over the other monomers. This is their much greater stability to air and moisture which allow them to be handled outside of a drybox during workup.

The reaction shown in method (4) provides a very good synthesis of sodium and potassium salts. This involves treatment of the thiophenol with a sodium-naphthalene complex for sodium salts and a potassium-anthracene complex for potassium salts. The complexes are very readily prepared and react instantly with the thiophenol. Further work showed that reduction of the appropriate disulfide to the substituted thiophenol was unnecessary when using the complexes since the complex was capable of a selective reduction of the disulfide bond yielding the desired salt (5).

Reaction (5a) illustrates an alternate means of obtaining the cuprous salt. This procedure suffers only from contamination of the monomer by unreacted copper metal while that in reaction (3) suffers from impurities in the cuprous oxide.

In an effort to determine which of the two syntheses for copper salts (3) or (5a) was preferable, an extensive investigation of them was made. This involved preparation of large batches of monomer by each technique. Portions, then, from each source were extracted with acetone, sodium hydroxide, or ammonium hydroxide in an effort to remove impurities. Acetone extraction seemed to result in no improvement as shown by monomer analysis and polymerization results. The other two extractants either removed the copper producing bis-(p-bromophenyl) disulfide (ammonium hydroxide extraction) or degraded the monomer (sodium hydroxide extraction).

In spite of the negative extraction results, it was determined that the best synthesis involved the reaction of the disulfide with fresh copper dust. This was indicated by elemental analysis of the monomers and the superior results obtained in polymerization of this monomer. A comparison of the polymers obtained from polymerization of the monomers from the two sources for nine days in the solid state at 212°C is given in Table V.

It might be mentioned that the lower melt viscosity shown for crude polymer made from the monomer in column 2 of Table V probably results from the lower percentage of crosslinked material present and therefore indicates greater linearity in this polymer. It is also of importance that the relative viscosity for this polymer was the highest observed for any of the polymers investigated.

Since the disulfide-copper dust reaction was shown to be preferred for future synthesis, it was desired to determine

TABLE V

Polymerization of Copper Salt Monomers

at 212°C in the Solid State

Monomer Source	Reaction (3)	Reaction (5a)
M.P. (°C)	276-280	285-288
Yield	76.0%	88.4%
$\eta_{303(\text{poises})}$ Crude	6×10^4	2×10^4
Diphenyl Ether Solubles	1×10^3	1×10^3
Insolubles in Crude	24.0%	11.6%
η_{rel} (of Diphenyl Ether Solubles)	1.187	1.201

if ultraviolet light catalyzed the reaction. Some evidence indicating that this was a possibility was obtained with an ultraviolet lamp in earlier experiments. Therefore a small scale reaction was irradiated with a sunlamp which produces 23% of its light in a wide range of the ultraviolet region. Therefore it would probably give off the particular frequency of radiation that would catalyze the desired reaction. This probably did occur, but in addition frequencies catalyzing degradation reactions must also have been emitted because the reaction mixture soon became a black tarry mass.

Since the purity of the monomer would also depend on the purity of the starting materials, an attempt was made to find better techniques for the purification of bis-(p-bromophenyl) disulfide. Sublimation and steam distillation proved to be unsuccessful. Recrystallization, however, is very satisfactory. The best solvents appear to be ethanol, acetone, and petroleum ether.

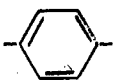
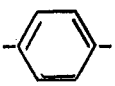
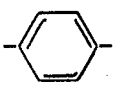
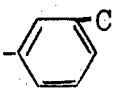
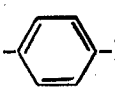
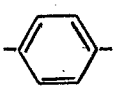
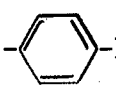
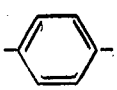
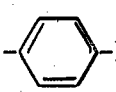
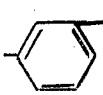
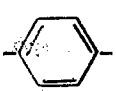
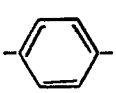
Listed in Table VI are the various monomers synthesized along with the monomer purities and the overall yields from the starting materials. In the four cases showing yields of less than 90% the cause is in the substituted thiophenol synthesis with the exception of lithium p-bromothiophenoxide. In this case the low yield is due to the lithiation reaction.

Some explanation concerning the entries for the copper salt purities is needed. Since the insolubility of the copper monomers eliminated most analytical methods for purity determinations and since elemental analysis was not accurate enough to give precise values, the purity of these materials were not known more exactly than indicated in Table VI. However, it is believed from polymerization results that these monomers must be very close to 100% purity.

The last two entries in Table VI are examples of monomers, which would be used in an A-A, B-B condensation system where the B-B monomer would be a p-dihalobenzene. These disalts were prepared in the manner shown in Figure 6. The p-dibromobenzene is treated with the product from the reaction of sodium-naphthalene complex with diethyl disulfide in the presence of copper dust namely sodium ethylmercaptide. This results in the formation of 1,4-bis(ethylthio)benzene. The bis-sulfide so formed is cleaved by sodium in liquid ammonia to give, on acidification, 1,4-benzenedithiol. Treatment of the 1,4-benzenedithiol with n-butyllithium results in the dilithium salt. Alternatively the 1,4-benzenedithiol can be treated with sodium-naphthalene complex to give the disodium salt in the yields and purities shown in Table VI.

TABLE VI

Results of Monomer Preparations

Monomer	Overall Yield %	Purity %
LiS-  -Cl	95.0	96.3
LiS- -Br	37.0	90.0
NaS-  -F	50.5	98.8
NaS-  -Cl	95.0	97.2
NaS-  (Cl)	95.0	98.0
NaS-  -Br	91.0	96.5
NaS-  -I	30.0	100
KS-  -Br	92.5	100
CuS-  -Cl	97.9	>95.0
CuS-  -Br	99.0	>95.0
CuS-  (Br)	36.2	>95.0
LiS-  -SLi	68.0	96.0
NaS-  -SNa	93.0	100

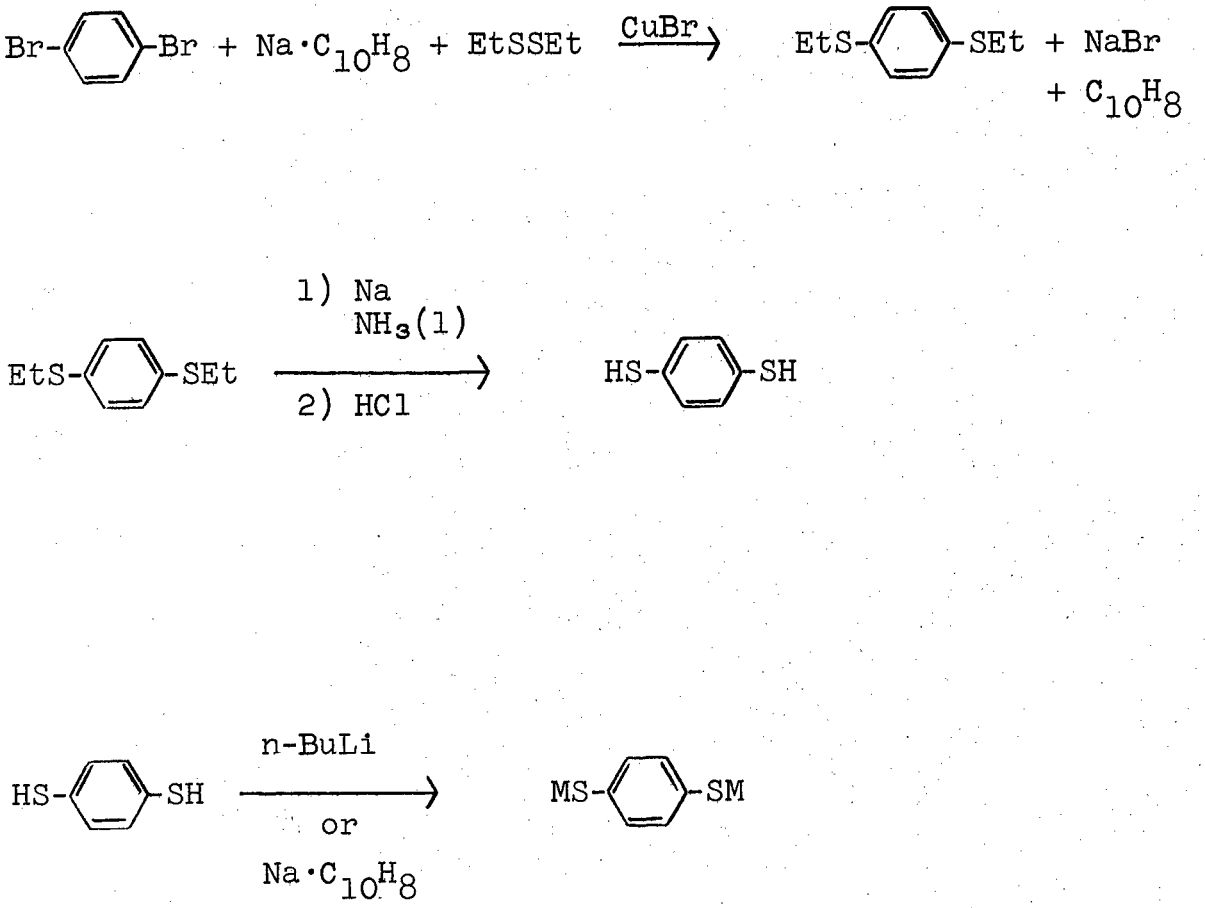


Figure 6. DISALT SYNTHESIS

Polymerization

Once the monomers had been synthesized, their polymerization reactions were studied. The ampoules were prepared by the same general technique used in the kinetic studies. The workup, however, was somewhat different. After the ampoule was cooled and opened, the contents were extracted twice with boiling water, and the water extract was titrated potentiometrically for halide ion with silver nitrate to determine the monomer conversion. The residue was heated to reflux in diphenyl ether. Then the resulting solution was filtered, and the filtrate poured into cold methanol to precipitate the polymer. The precipitate was filtered off, washed with acetone and dried under vacuum at 80-120°C for several hours. Yields were based on the vacuum dried polymer obtained.

An alternate workup which allows the isolation of crosslinked insoluble polymer is as follows. The contents of the ampoule were extracted with ammonium hydroxide until no further blue color was obtained. This removed the cuprous bromide formed in polymerization and left as a residue the soluble and insoluble polymer. The polymer then could be used as such or extracted with diphenyl ether and re-precipitated as above. Yields were based on the same criterion as that used for the other method of workup.

Polymerizations were carried out in the solid state or in solution. It was found earlier that if the monomer was polymerized above its melting point in the absence of solvent an uncontrollable reaction ensued leading to a black charred mass. The maximum temperature that could be used was 10-15° below the monomer melting point. The usual temperatures employed were 200° and 250°C. The solid state polymerization appears to be just that. In no instance was the presence of liquid observed and the particle size of the material in the ampoule appeared to be unchanged. The only visual change appeared to be a very slight change in color.

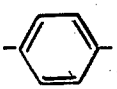
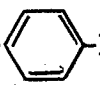
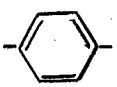
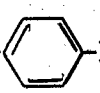
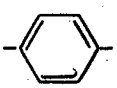
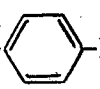
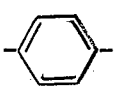
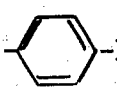
The solution reactions were run in quinoline, diphenyl ether and pyridine at about 1 M concentration. Pyridine seemed to give the best results and showed a fifty fold enhancement in rate over the solid state reactions at the same temperatures.

Two types of monomer systems were investigated, the A-A, B-B and the A-B. In the first system there is one inherent disadvantage; the two monomers must be present in exactly stoichiometric quantities to achieve a high molecular weight polymer. With the A-B monomers this is automatically taken care of due to the nature of the monomer.

In the A-A, B-B system, two different monomer sets have been briefly considered. The results are given in Table VII. In the case of the dilithium salt a low yield of low melting polymer was obtained. With the disodium salt very little, if any, polymeric material was obtained.

TABLE VII

A-A and B-B Polymerizations
250° Pyridine Solvent

A-A	B-B	Time (hrs)	Polymer Yield %	M. P. °C
LiS-  -SLi	Br-  -Br	6	39	220-230
NaS-  -SNa	Br-  -Br	1	7	>100
NaS-  -SNa	Br-  -Br	6	6	>100
NaS-  -SNa	Br-  -Br	12	8	>100

Some results from the kinetic studies could shed some light on the above results. When sodium thiophenoxide was heated in pyridine for twelve hours at 250°C no apparent reaction occurred. When p-dibromobenzene was treated under the same conditions a black insoluble, infusible mass was obtained. Therefore what may be occurring is that, due to the low reactivity of the disodium salt, the pyridine is degrading the p-dibromobenzene before any appreciable amounts of polymer can be formed. However, the more reactive dilithium salt reacts with the p-dibromobenzene to give some polymer before the pyridine degradation reaction becomes dominate.

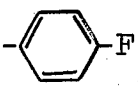
Since the A-B system has a built in stoichiometric balance, since it is easier to prepare, and since the results have been much better with this system than with the A-A, B-B system the A-B monomers have been studied more extensively.

One of the monomers studied was sodium p-fluorothiophenoxide. The results are given in Table VIII. Although the first two runs are at somewhat higher temperatures than is usually employed, their results are quite interesting. As has been mentioned previously fluoroderivatives have a potentiality for preferential polymer formation. In the first two runs we have some evidence which bears on this question. Condensation polymerization theory predicts that for conversions of 58% and 79% the number average degree of polymerization, $\overline{x}_n$, obtained for the polymers would be 2 and 3 respectively. However, the $\overline{x}_n$'s observed were 9 and 7 respectively. This may be an indication that preferential polymer formation is taking place.

Tables IX and X show the results for two more monomers, the sodium and potassium salts of p-bromothiophenol. The results in Table IX exhibit several interesting features. One is the effect of pyridine that was mentioned before, a fifty fold enhancement in rate over the solid state reaction. Another is the rate enhancement of pyridine over quinoline. In addition it might be noted that the percent of bromine continues to decrease, indicating continued polymerization, even after titration of liberated bromide ion indicates a complete reaction. One feature of distinct importance is the fact that $\overline{x}_n$ reaches a maximum, at 24 hours, and then decreases. This apparent decrease in molecular weight after an optimum reaction time appears in all of the polymerizations studied and is signalled by a drop in melt viscosity, melting point and yield. Table X shows both the drop in melting point and yield occurring after 24 hours reaction time.

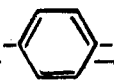
Table X also shows two other features of interest. One is the lack of catalytic effect of cuprous bromide as shown by runs 7 and 8 versus 3 and 4. The other is a temperature effect on the rate as shown by the last two runs. This latter effect amounts to a sixteen fold decrease in rate for the 50° drop in temperature.

TABLE VIII

Polymerization of NaS-  -F

Time (Hrs)	Temp. °C	% Conversion	M. P. °C	$\overline{DP}_F$	System
2	320	58.0	~265	9	Pyridine
72	320	79.0	>300	7	Solid State
6	250	91.0	272-280	-	Pyridine

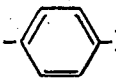
TABLE IX

Polymerization of NaS-  -Br at 250°C

Solvent	Time (hrs)	% Conversion	Polymer % Br	Polymer % S	Polymer M. P. °C	$\overline{DP}_{Br}$
None	36	79.2	-	-	-	-
None	140	93.0	-	-	-	-
Quinoline*	24	91.3	-	-	-	-
Pyridine	1	72.0	13.2	31.3	160-200	5
Pyridine	2	97.8	6.00	28.9	240	12
Pyridine	3	97.6	3.75	27.1	240-250	19
Pyridine	6	100.0	1.50	29.1	260	48
Pyridine	12	100.0	0.67	29.4	265	112
Pyridine	24	100.0	0.58	29.0	-	126
Pyridine	36	100.0	0.69	29.2	265	107

*Reaction Temperature 280°C.

TABLE X

Solution Polymerization of KS-  -Br

Temp. °C	Time (hrs)	% Conversion	% Polymer	M. P. °C	$\overline{DP}$*
250	1	80.7	-	~260	-
250	2	90.6	-	~264	20
250	3	100.0	-	~265	36
250	8	100.0	55	262-269	33
250	24	100.0	77	257-263	78
250	36	100.0	60	238-245	202
250	3**	100.0	54	263-268	38
250	8**	100.0	47	260-265	32
200	38	92.3	64	262-266	17
200	53	92.5	59	263-268	18

*$\overline{DP}$ from Br end group analysis

**CuBr added

Table XI summarizes the results of the preliminary studies on all the A-B type monomers investigated. The yields given are the maximum polymer yields obtained with the particular monomer. The melting points are also maxima and give an indication of relative molecular weights attained in each case. The last statement is true since we have found that the higher the melting point the higher average molecular weight up to the crystalline melting point of the polymer, 287°C. The rate constants are overall constants based on second order kinetics.

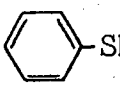
From the first four entries it can be seen that the ease of halogen displacement is essentially the same as that found in the model reactions namely I>Br>F>Cl. In addition it can be seen that the best polymer, as indicated by melting point, resulted from the p-fluoro and p-bromothiophenoxides with the p-bromo giving the best yield.

From the third, fifth, sixth and seventh entries it can be seen that the effect of the cation on the rate is also the same as that found in the model reactions being Cu>Li>Na>K. In this set of entries, however, cuprous p-bromothiophenoxide has by far the best yield and melting point. In fact these values are the best of all those obtained. Consequently the monomer chosen for further study was cuprous p-bromothiophenoxide. This is the same monomer that the kinetic studies indicated to be the preferable one.

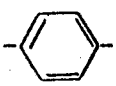
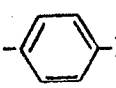
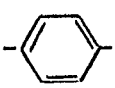
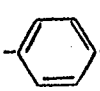
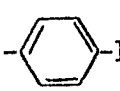
Cuprous p-bromothiophenoxide, therefore, was extensively studied under four different reaction conditions. These were 200° and 250°C in the solid state and in pyridine. The results are given in Figures 7-10. The solid line represents the yields observed while the dashed line refers to the melting points. In each case a maximum is reached after a given reaction time beyond which the yield and the melting point decrease. These maxima in melting point and yield are 280°C and 90% yield for five days at 200°C in the solid state; 278°C and 78% for two and one-half days at 250°C in the solid state; 278°C and 95% yield for 32 hours at 200°C in pyridine; and 287°C and 90% yield for 16-32 hours at 250°C in pyridine. From these results the best polymerization conditions would appear to be 16-32 hours at 250°C in pyridine or five days at 200°C in the solid state.

Therefore when a scale up on the polymerization reaction was desired, 16 hours at 250°C in pyridine was selected for the reaction conditions. The first attempts were carried out in glass-lined high pressure reactors. In each case, however, the liner broke and low yields resulted. In addition to the low yield, the bomb temperature could not be measured any closer than 50-60°C in the second experiment since the thermowell had to be removed. Consequently the polymer in this case was very

TABLE XI

Polymerization of (p)X-  -SM

At 250°C in Pyridine

Monomer	Polymer % Yield	M. P. °C	k_2
NaS- -F	63	272-280	0.026
NaS-  -Cl	62	245-260	0.011
NaS-  -Br	75-80	260-265	0.13
NaS-  -I	42	225-240	1.01
LiS-  -Br	20	243-248	2.57
KS-  -Br	80	265-269	0.096
CuS- -Br	97	283-287	>3.0

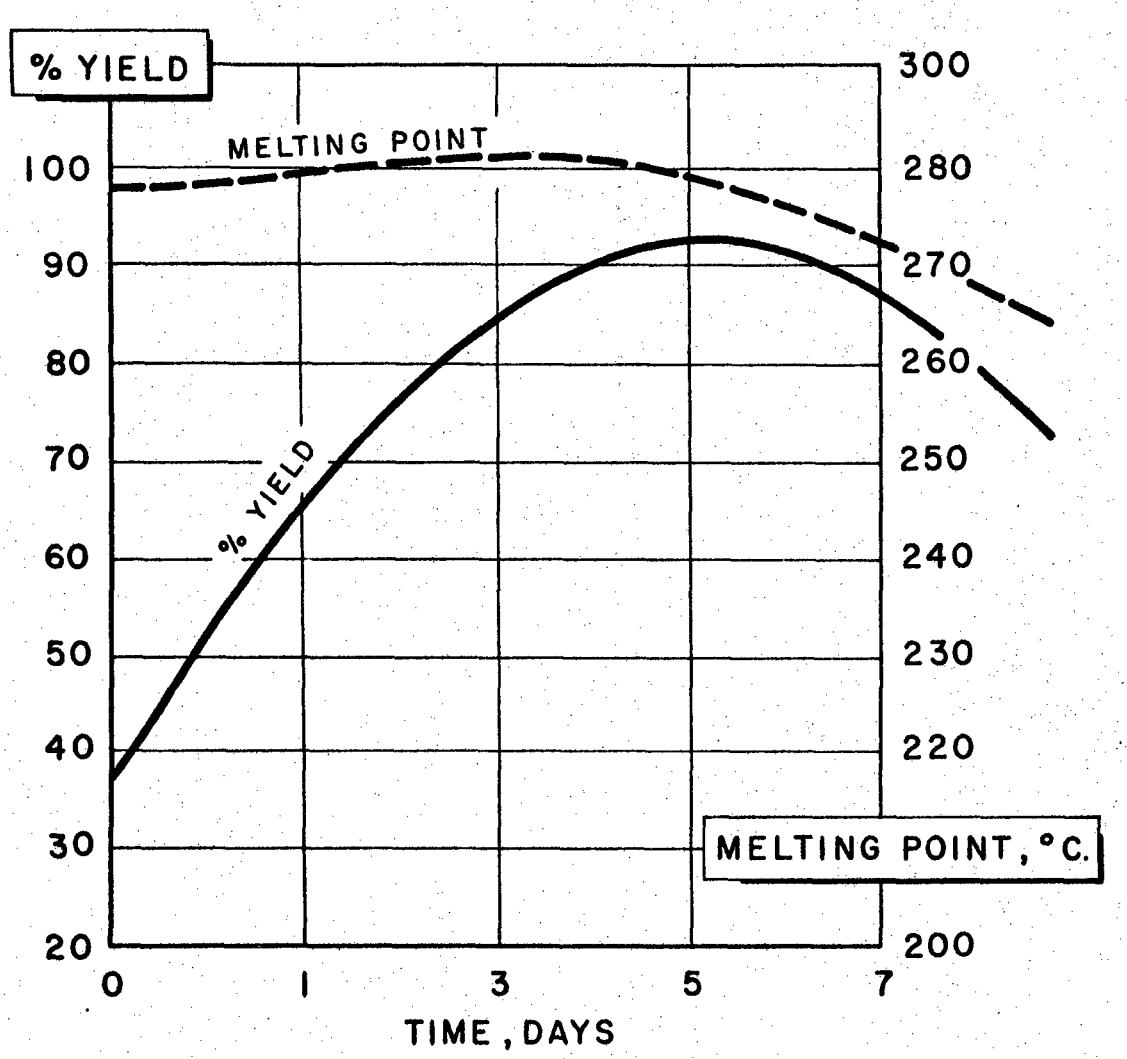


FIGURE 7. Br ϕ SCu, SOLID STATE, 200°C.

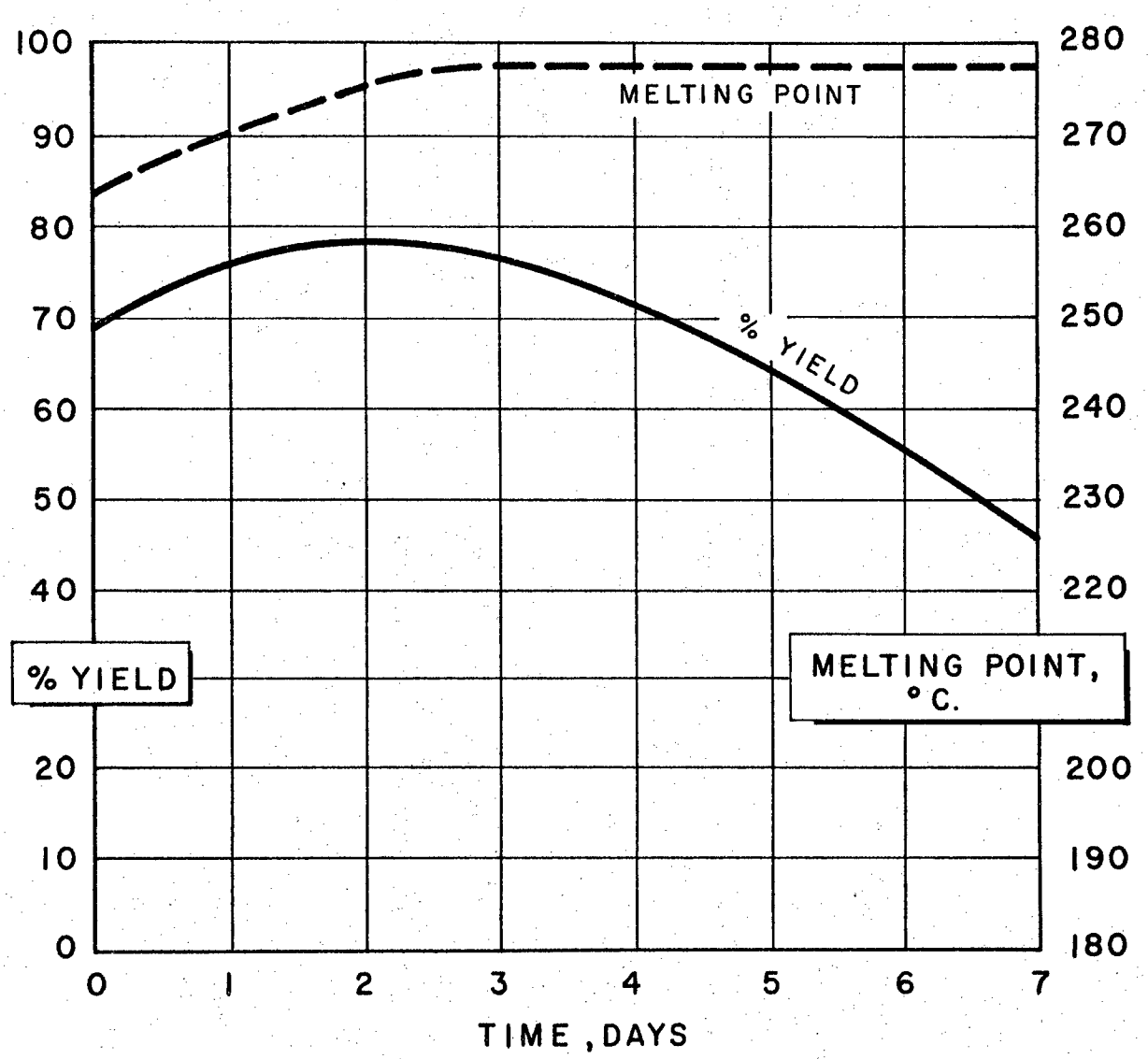


FIGURE 8. CuS ϕ Br, SOLID STATE, 250°C.

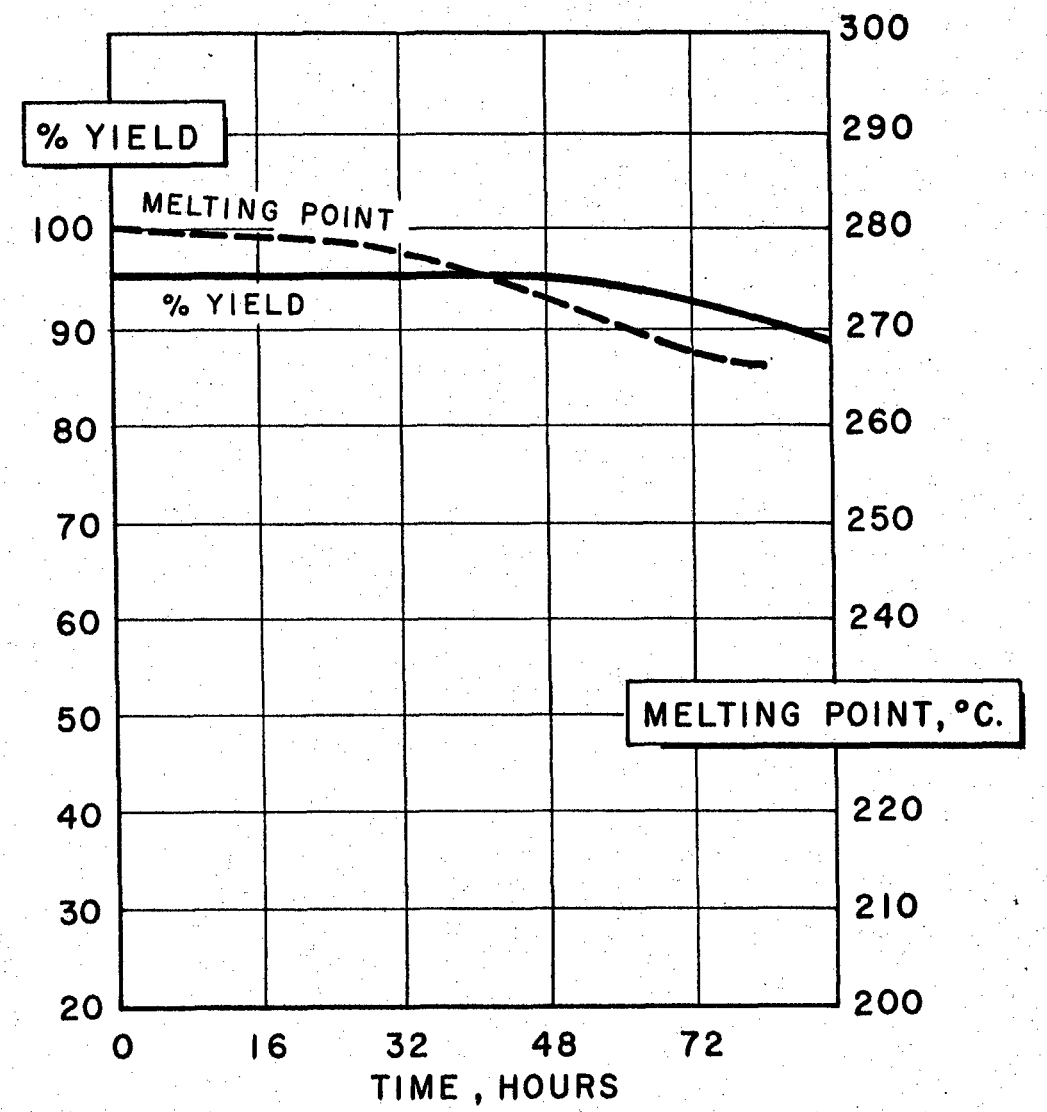


FIGURE 9. BrϕSCu, PYRIDINE, 200°C.

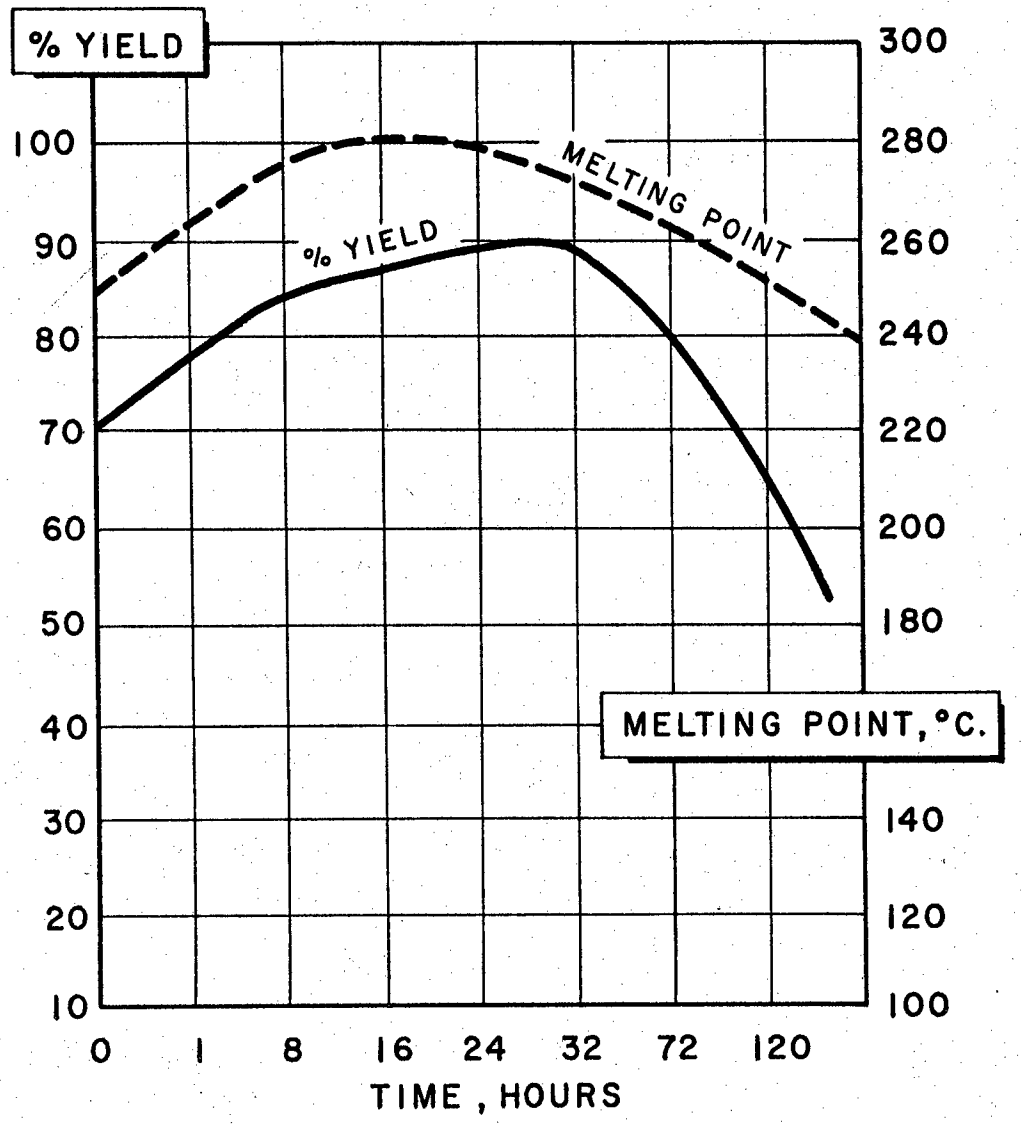


FIGURE 10. Br ϕ SCu, PYRIDINE, 250° C.

poor, as indicated by the melting point, undoubtedly due to too low a reaction temperature.

In order to avoid the difficulties, at least temporarily, of the solution polymerizations, it was decided to polymerize at 212°C in the solid state. The last three runs in Table XII show the results of this work. The runs were made for five, six and one-half, and nine days. The fact that reaction times greater than five days were needed to obtain a polymer with good properties, run 5, is probably due to the lack of agitation in the ampoules. This would probably cause a temperature gradient in the reactants from 212°C on the outside of the ampoule to much less than 200°C in the center. After prolonged reaction times this gradient would disappear, but the overall reaction would be slowed down.

In addition to the polymerization studies a preliminary investigation of repolymerization of low molecular weight material was made. From the elemental analyses of the polymers it was discovered that the amounts of copper and bromine in the polymer were about equal. This suggested that the polymer end groups remained intact during workup. Consequently it should be possible to polymerize the polymers further by subjecting them again to polymerization conditions. The results of these attempts are given in Table XIII. It can immediately be seen from the melting points that essentially no change has taken place under any of the conditions used. However, some increase in molecular weight is indicated by an increase in solution viscosity (Figure 15).

Polymer Properties

During the course of the polymerization studies the properties of the polymers produced were investigated. Much of this investigation was concerned with molecular weight determinations on the polymer. From the scatter observed in the percent sulfur in the polymer, Table IX, it can be seen that sulfur analysis is of no use for molecular weight determinations. The percent bromine is useful for determinations at lower molecular weight, Table IX, but as would be expected it fails at higher molecular weight. Therefore it was decided to investigate the melt viscosity of the polymers.

The apparatus used is shown in Figure 11. The polymer is packed into the capillary in the viscometer so as to give a bubble-free column. The side arm on the tube is for introduction of a vacuum or an inert gas. The calibration lines on both tube and plunger serve as a means of timing the plunger drop. The plunger has a narrow tip which slides into the capillary as well as a cap on which weights can be placed.

TABLE XII

Large Bomb Polymerizations

Time (Hrs)	Temp. °C	Solvent	% Yield	M. P. °C
15-1/2	250	Pyridine	52.7	278-285
16	250	Pyridine	78.7	255-265
120	212	None	71.8	259-260
156	212	None	61.7	264-274
216	212	None	>95.0	279-290

TABLE XIII

Repolymerization

Temp. °C	Time (hrs)	Solvent	% Yield	M. P. °C
250	0	Pyridine	-	265-278
250	12-1/2	Pyridine	62.4	265-275
250	12	Pyridine	69.3	275-282
200	0	None	-	265-272
200	24	None	94.0	255-270
200	72	None	89.7	265-273

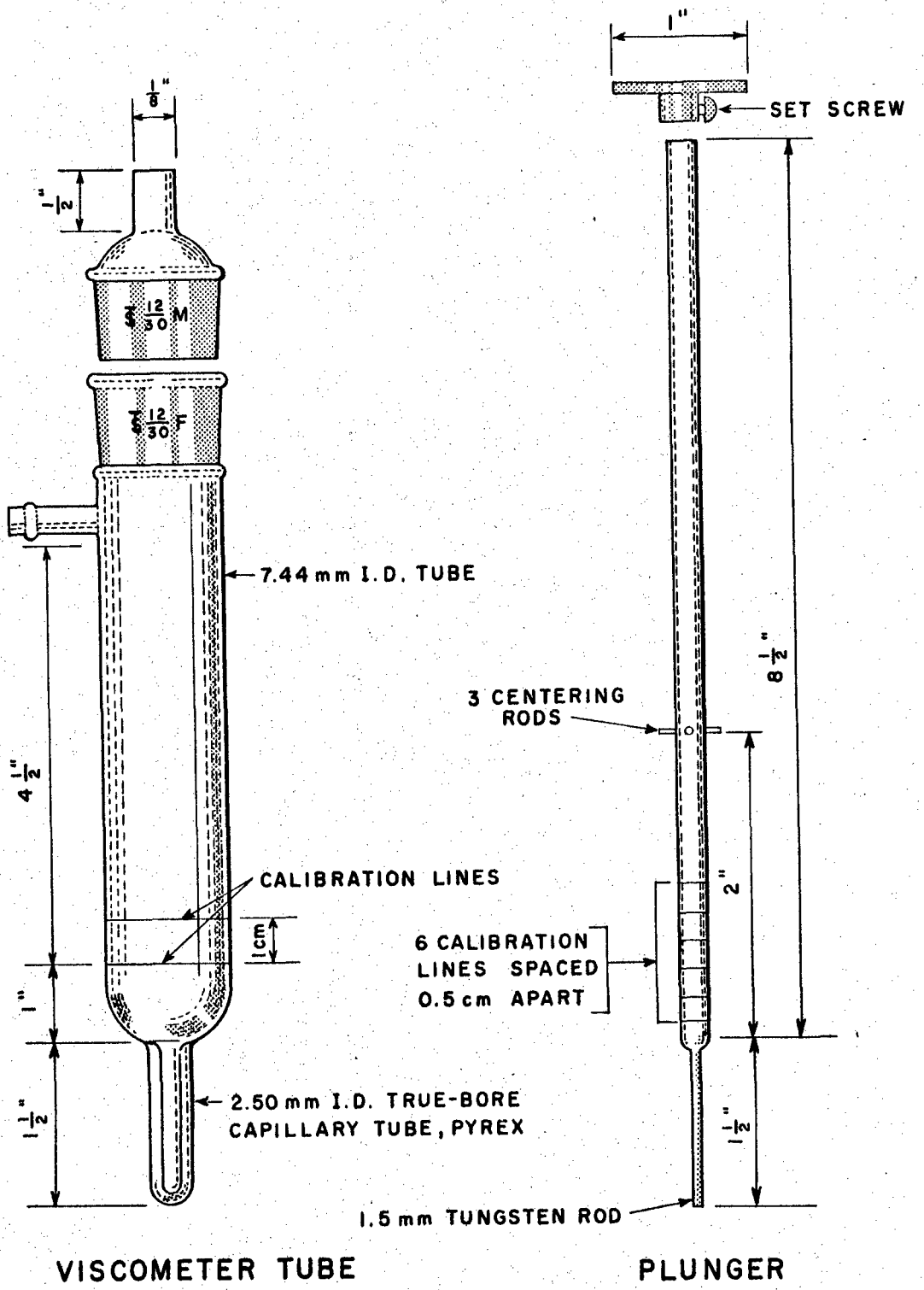


FIGURE 11. MELT VISCOMETER

The heating apparatus for the viscometer is shown in Figure 12. The central well is used for the viscometer and the two thermowells for determining the temperature at both ends of the capillary tube in the viscometer. The temperature in the center well was calibrated against thermometers in both thermowells in order to provide two independent measures of the center well temperature.

Since viscosity determinations are capable of giving only relative molecular weights, it was necessary to calibrate the technique. This was done by determining the viscosities of polymers whose bromine analyses were believed to be reliable.

The results of the melt viscosity determinations at 303°C are given in Figures 13 and 14 for solution polymerizations at 200° and 250°C and for solid state polymerizations at 200° and 250°C respectively. In each case the viscosity rapidly increases to a maximum and then falls off about as rapidly. The maxima occur at 8000 poises for 32 hours at 200°C in pyridine, 230,000 poises for 16 hours at 250°C in pyridine, 26,000 poises for 5 days at 200°C in the solid state, and 6000 poises for 3 days at 250°C in the solid state. The highest two maxima 230,000 poises and 26,000 poises correspond roughly to $\overline{x}_n$'s of 400 and 200 respectively. In larger scale reactions in the solid state at 212°C the maximum is much less pronounced and occurs at 9 days instead of 5 days. The melt viscosity at the maximum was about 2000 poises which corresponds to an $\overline{x}_n$ of 100. This is somewhat lower than the values listed above but the relative viscosity, 1.201, is the highest ever obtained. These maxima all occur at about the same regions in reaction time that polymer melting points and percent yields show maxima. Apparently some degradation process is taking place which becomes dominate after the polymerization reaction has slowed down. In addition infusible, insoluble materials are found at prolonged reaction times indicating a crosslinking reaction. The fact that the appearance of maxima occurs in both solution and solid state polymerizations would indicate that pyridine is not responsible for the degradation. The actual culprit may be the salt produced during polymerization. This is suggested by the data in Figure 15. These are the results of solution viscosity determinations on repolymerization reactions. As can be seen no maxima occur. Instead the viscosity rises steadily with increasing reaction time. Since on workup of the polymer prior to repolymerization the halide salt was removed, this would seem to indicate that this material may indeed be the culprit.

In addition to the melt viscosity work, solution viscosities have also been determined. These were carried out on a 1% polymer solution in diphenyl ether at 250°C. The results in general correlate quite well with the melt viscosity results. However,

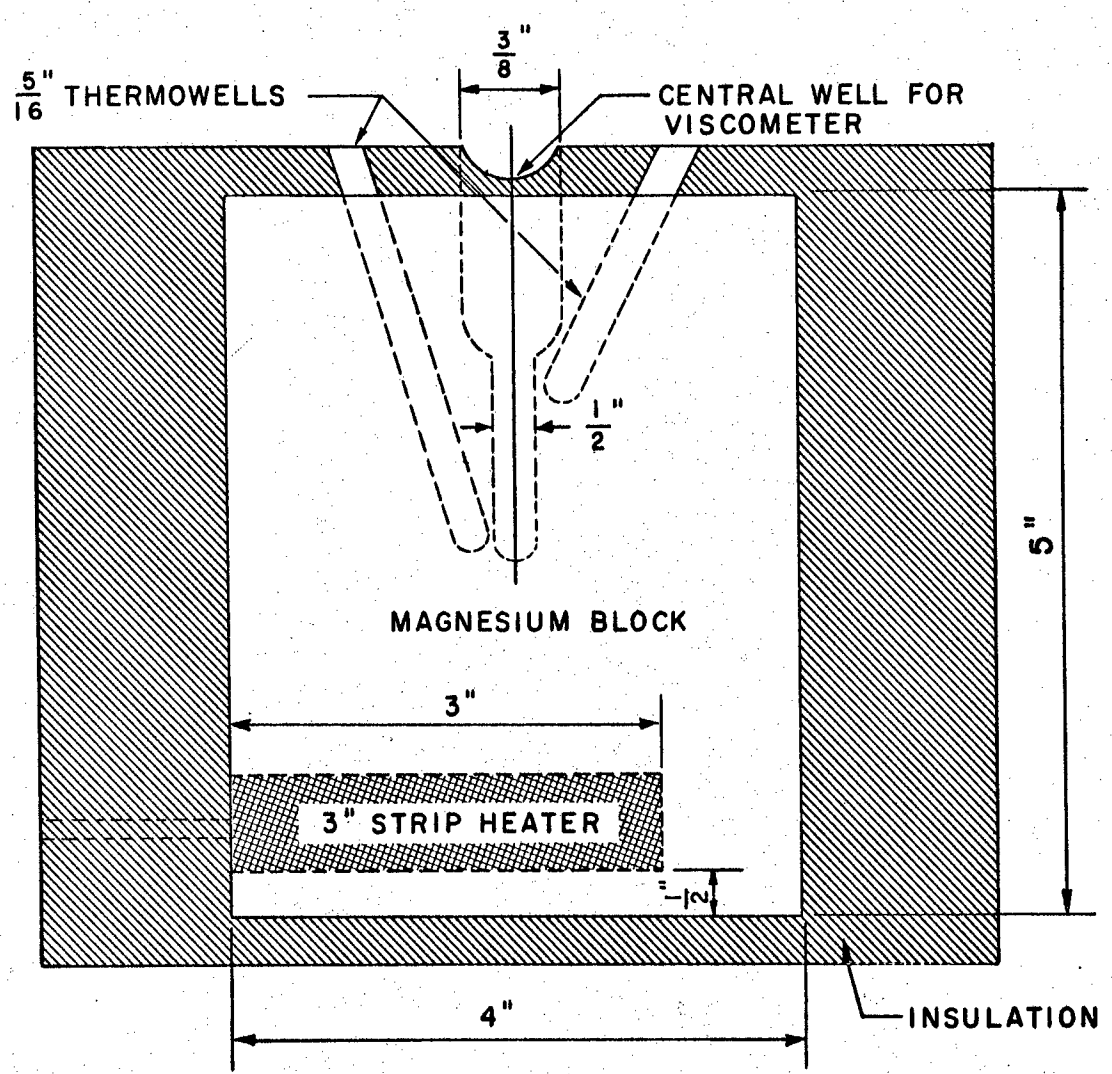


FIGURE 12. **HEATING BLOCK FOR VISCOMETER**

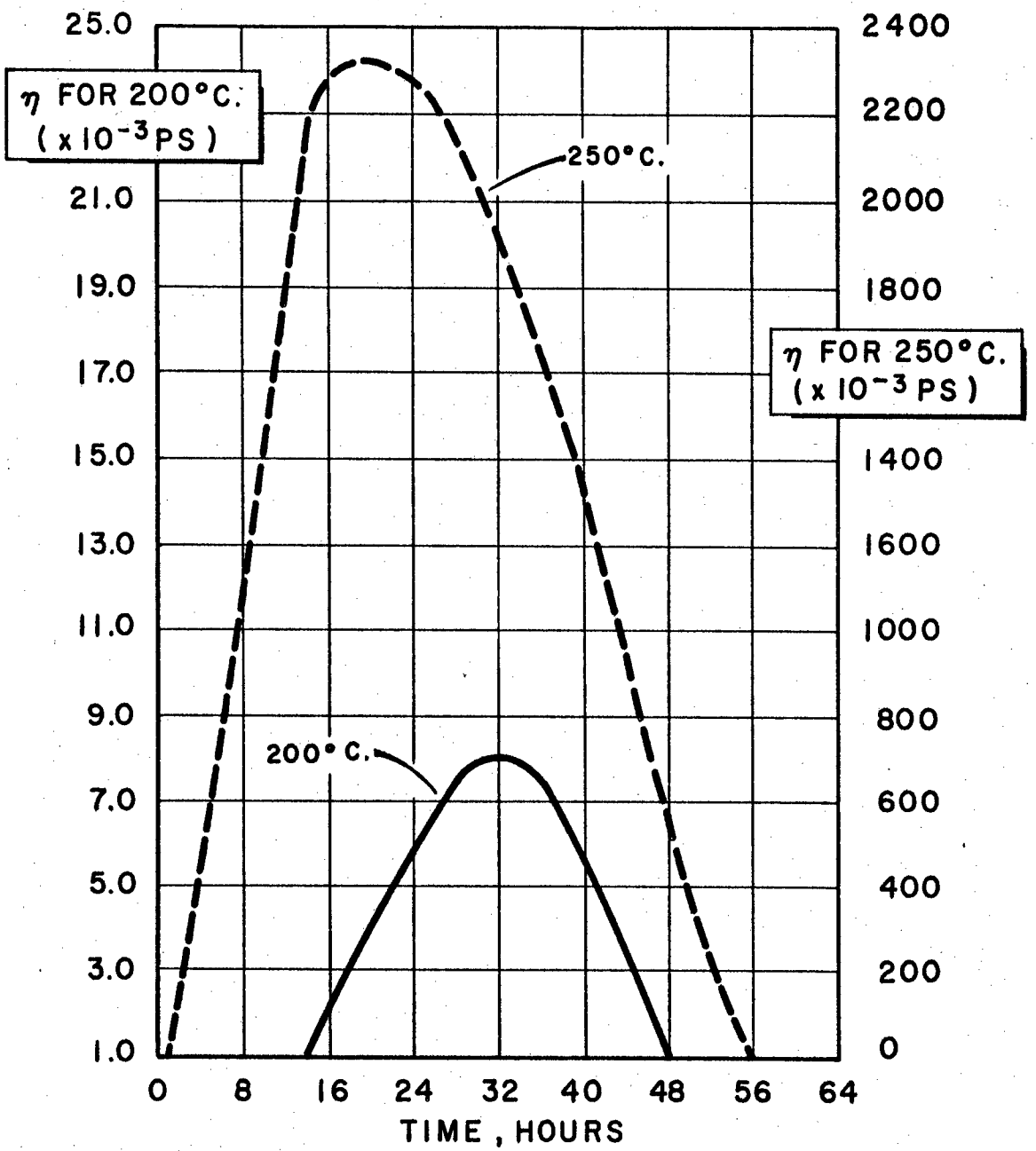


FIGURE 13. MELT VISCOSITY–POLYMERIZED IN SOLUTION

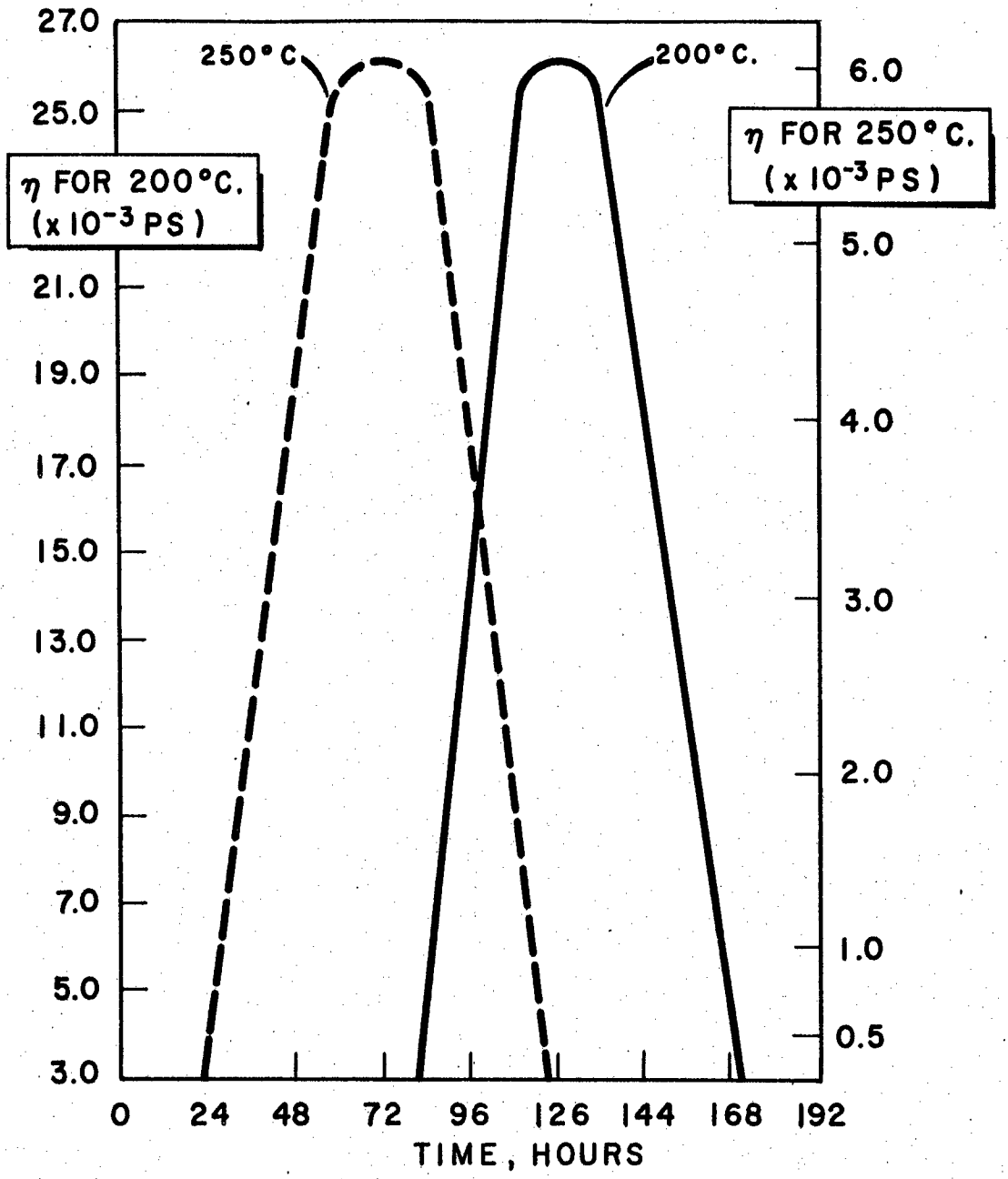


FIGURE 14. MELT VISCOSITY-POLYMERIZED IN SOLID STATE

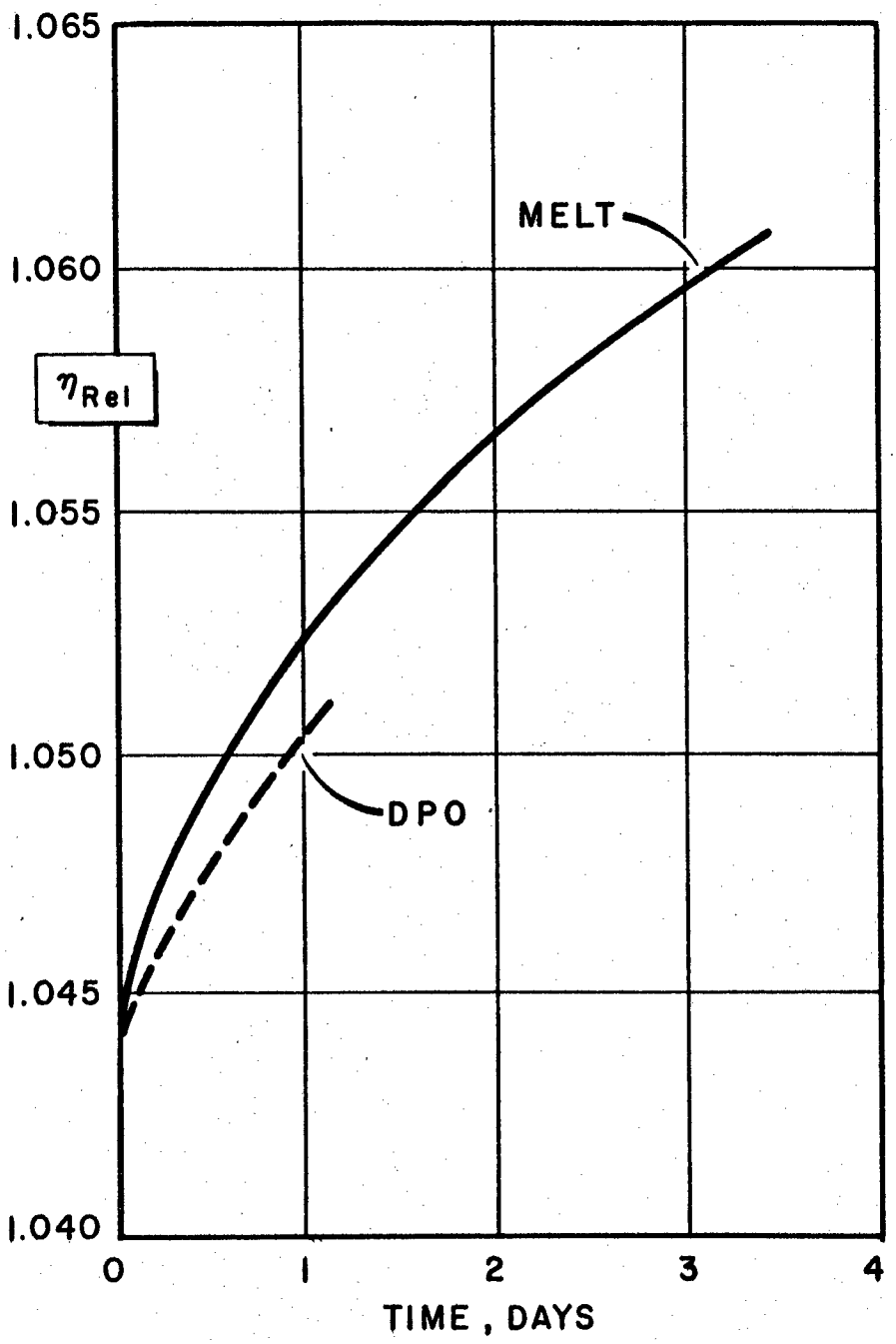


FIGURE 15. SOLUTION VISCOSITY–REPOLYMERIZATION

this technique has one advantage in that it can be used to classify polymers as to molecular weight whose melt viscosity is too low to measure.

Another property investigated was the solubility of the polymer. Since phenylene sulfide polymer is a highly crystalline material, a high boiling solvent is required. The results of solubility tests with such solvents is given in Table XIV. The polymer is insoluble in the first four solvents listed, and it reacts with sulfuric acid. In diphenyl ether and diphenyl sulfide, however, at least a 1% solution can be attained at reflux. The polymer, due to its crystalline nature, then precipitates on cooling at about 200°C in diphenyl ether and somewhat lower, 170°C, in diphenyl sulfide. It is the solubility of the polymer in diphenyl ether which made solution viscosity determinations possible as well as providing a means of separating the polymer from the other products of polymerization.

A preliminary investigation of the fabrication properties of the polymer was also made. It was found that a fiber could be pulled from the melt of a polymer of high enough molecular weight. This fiber was fairly strong and flexible.

Somewhat more time was spent on the compression molding properties. The higher molecular weight materials could be molded into a fairly tough, flexible film that was at least partially transparent. The film could be folded and creased without cracking. An additional property was noted during the molding operations. This was the great tenacity with which the polymer adhered to the metal molding plates or to glass. In one case the polymer stripped the metal coating from the plate instead of breaking free from it. The polymer did not adhere to Teflon, but the color and transparency of the film were much worse when Teflon was used as a molding plate.

One of the most important properties investigated was the thermal stability of the polymer. Figure 16 shows the results of the thermal gravimetric analysis of some polymer samples sent to Wright-Patterson Air Force Base for testing. Under either air or nitrogen polyphenylene sulfide is stable to about 450°C. At this point degradation sets in slowly until, in air, the polymer is essentially gone at 700°C. In nitrogen, however, degradation appears to cease at 600°C., and a thermally stable residue is formed which resists further degradation up to 900°C.

Since it would be very desirable to know if this thermally stable residue has useful properties, several samples were treated at 400°C and 500°C under nitrogen to determine what properties the residue did have. The results are given in Table XV. In each case a black glassy material was obtained which probably was

TABLE XIV

Solubility of Phenylene Sulfide Polymers

Solvent	Solubility at Reflux	Precipitation Temperature
Pyridine	0.0%	-
2,4-Lutidine	0.0%	-
Toluene	0.0%	-
Polyether	0.0%	-
Diphenyl Oxide	>1.0%	200°C
Diphenyl Sulfide	>1.0%	170°C
H_2SO_4	Reacts	-

TABLE XV

Heat Treatment of Low Molecular Weight Polymer

Starting Polymer	Time (hrs)	Temp. °C	M. P. °C	Weight Loss %	Diphenyl Ether Solubility %	Film Properties		
						Toughness	Adherance	Appearance
Polymer 1	0	-	265-270	-	100	Very poor	Very poor	Opaque
	3	500	>600	30	0	Good	Very good	Transparent
	24	500	>600	56	0	Too high melting and brittle		
	20	400	283-287	16	99	Very poor	Very poor	Opaque
	40	400	285-290	22	99	Fair	Good	Transparent
	68.5	400	>600	27	0	Very good	Very good	Transparent
Polymer 2	0	-	262-265	-	100	Poor	Poor	Opaque
	3	500	>600	38	0	Good	Good	Transparent
Polymer 3	0	-	264-274	-	100	Very poor	Very poor	Opaque
	70	400	>600	18	0	Excellent	Excellent	Transparent
Polymer 4*	0	-	279-285	-	100	Poor	Fair	Semitransparent
	74	400	>600	15	0	Excellent	Excellent	Opaque-transparent

* Contains crosslinked material.

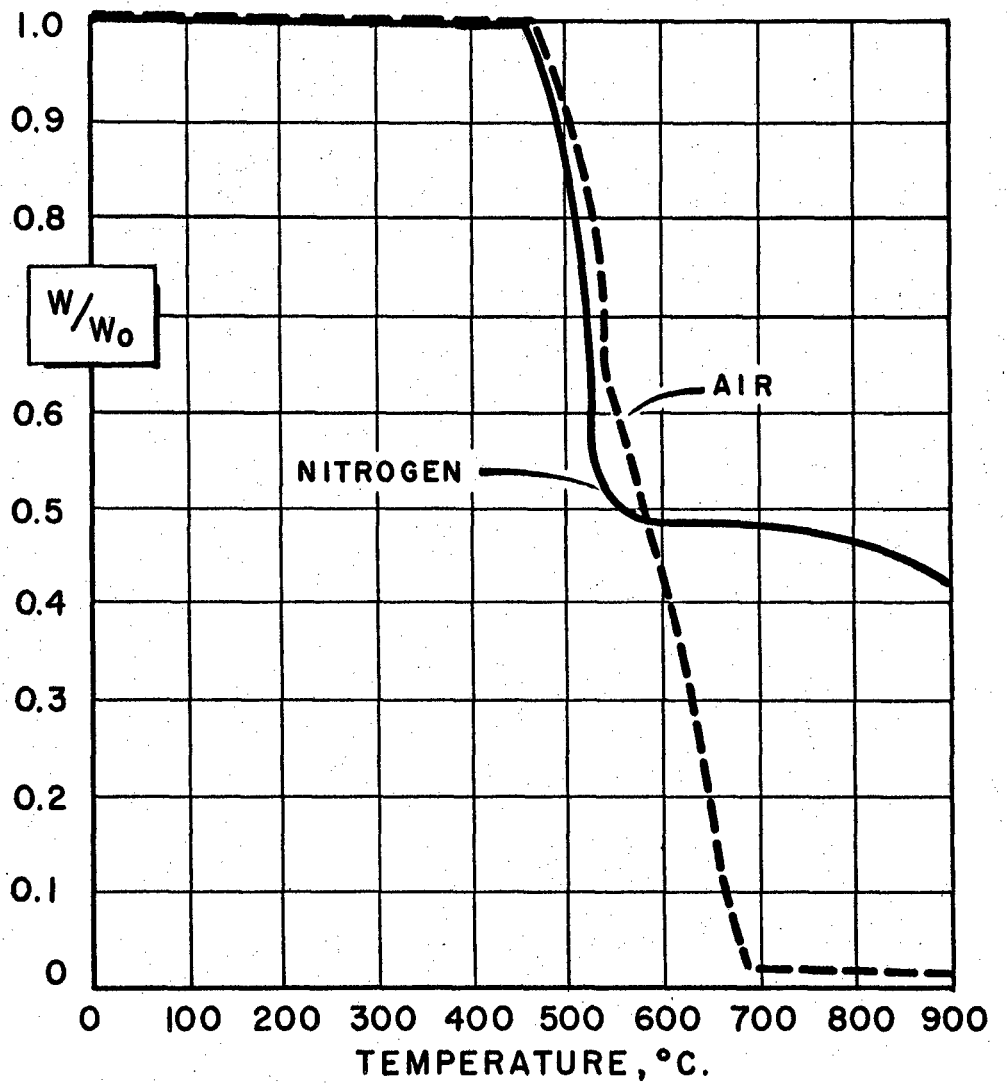


FIGURE 16. THERMAL GRAVIMETRIC ANALYSIS

crosslinked. The best material resulted from treatment at 400°C for 68-74 hours which gave a material with better properties than the original material even though some degradation had occurred. Treatment at 500°C for prolonged periods of time seems to be too drastic resulting in a material with poor molding properties. After only three hours at 500°C, though, the material still has good molding properties.

One interesting feature of the heat treatment was that material having good molding properties appeared only after solubility in diphenyl ether had disappeared. Thus the two runs that produced material that was still soluble in diphenyl ether gave only poor to fair films while the insoluble materials with the exception of that from 24 hours at 500°C gave good to excellent films.

Another interesting feature was the effect of molecular weight on weight loss and film properties. The molecular weights are roughly in the order polymer (4)>polymer (3)>polymer (1)> polymer (2). The weight losses for a given treatment time, however, are in the reverse order, polymer (2)>polymer (1)>polymer (3)>polymer (4). The film properties also appear to correlate with the molecular weight of the starting materials. In other words the material produced from the highest molecular weight starting material gave the best film and vice versa. It might be mentioned that the greatest improvement in properties came with those polymers having the poorest properties, but in all cases distinct improvements were observed.

Crosslinking Studies

A cursory investigation has been made of two reactions that could be used for crosslinking. Previous attempts have been made with sulfur which can lead to polysulfide bonds with their accompanying low thermal stability and with 1,4-benzenedithiol which can lead to crosslinked material by reaction with itself. Consequently new reactions were sought.

The first to be investigated involved treatment of the polymer with bromine at room temperature to introduce branch points and then allowing the brominated polymer to react with sodium sulfide. The bromination reaction resulted in the introduction of 83-90% of the theoretical number of aryl bromide groups. The subsequent condensation reaction then produced 95-100% of the theoretical numbers of crosslinks. The polymer treated with excess bromine gave a black powdery crosslinked product. The other attempt using 0.1 equivalents of bromine per repeating unit gave a usable polymer. However, the crosslinks were not uniformly distributed but were localized in 15-20% of the polymer. In addition to these two trials where the crosslinks were formed in pyridine at 250°C, an attempt was

made to crosslink a brominated polymer by molding it at 300°C for 20 minutes at 5000 pounds pressure with sodium sulfide. This resulted in a product with essentially the same properties as those from reaction in pyridine for 24 hours.

The second technique was one involving reaction with chlorosulfonic acid at 150°C to give sulfone crosslinks. Since no solvent was used, the crosslink density was not uniform, and the product was a mixture of polymer with varying degrees of crosslinking.

III. CONCLUSIONS

The following are the conclusions that can be drawn from our data:

(1) The kinetic studies indicate from the criteria of reaction rates, ease of preparation, and the order of by-product production that the monomer of choice would be cuprous p-bromothiophenoxide.

(2) Cuprous p-bromothiophenoxide can be synthesized most readily and in the purest state by the reaction of fresh copper dust with bis-(p-bromophenyl)disulfide.

(3) With the exception of four salts, all of the thirteen monomers studied can be prepared in greater than a 90% yield. In all but one case purities were very close to 100%.

(4) From comparisons of reaction rates of polymerization and polymer properties the monomer of choice is the one indicated in section (1) namely cuprous p-bromothiophenoxide.

(5) In all polymerizations optimum reaction times were observed where viscosity, yield, and melting point were greatest. The decrease in these quantities at longer reaction times is probably the result of degradation catalyzed by the salt produced. In larger scale reactions this problem does not appear to be as serious.

(6) Repolymerizations resulted in very little increase in molecular weight.

(7) Melt viscosity can be used to give an approximate value for the molecular weight of the polymer.

(8) Due to the solubility of the polymer in diphenyl ether at 250°C, solution viscosities can be obtained and are useful as a check on melt viscosities.

(9) The polymer has fairly good molding properties if the molecular weight is high enough. In all cases the molding properties are improved by heat treatment for 72 hours at 400°C under a nitrogen atmosphere.

(10) The thermal stability of the polymer produced from the copper salt is essentially the same as that indicated in the First Annual Report for the polymer from sodium p-bromothiophenoxide.

(11) The linear polymer can be crosslinked by reaction with bromine followed by reaction with sodium sulfide or alternatively crosslinking can be achieved by reaction with chlorosulfonic acid.

IV. EXPERIMENTAL

The experimental techniques used for the kinetic studies; the synthesis of the thiophenols, disulfides, and sodium salts; the polymerization studies; and the melt viscosity determinations are given in the First Annual Report, WADD Technical Report 61-139. The experimental techniques developed since then will be given below.

Monomer Synthesis

Lithium p-Chlorothiophenoxide. Into 100 ml of tetrahydrofuran in the dry box was placed 14.5 g (0.10 moles) of p-chlorothiophenol. To this was slowly added 27.3 g of a 23.4% solution of n-butyl lithium in n-heptane (0.10 moles). The salt was precipitated by addition of benzene, filtered off, and washed with benzene. Then it was redissolved in tetrahydrofuran, precipitated with ether, and dried on a high vacuum system for 24 hours at 100°C. Yield was 14.3 g. or 95%, M. P. 330-340°C. Purity was 96.3% as determined by titration with silver nitrate solution.

Lithium p-Bromothiophenoxide. This salt was prepared in 37.0% yield and 90.0% purity by the above method.

Dilithium Salt of 1,4-Benzenedithiol. This monomer was prepared as above using two moles of n-butyl lithium to one of dithiol. Yield was 68%, and purity was 96.0% by silver nitrate titration.

Cuprous p-Bromothiophenoxide. Method 1. A mixture was made up of 350 g (1.85 moles) of p-bromothiophenol, 118 g (0.825 moles) of 97% pure cuprous oxide, 300 ml of pyridine, and 4 l. of absolute ethanol. This mixture was placed in a 5 l. three-necked flask fitted with a Dean-Stark trap, a reflux condenser, a stirrer, and a nitrogen inlet and outlet. The reaction mixture was heated at reflux with stirring for 17 hours under a nitrogen atmosphere. The resulting mixture was filtered, washed with alcohol, washed with acetone, and then dried for 22 hours at 72°C. under a vacuum. Yield was 395 gms or 95%.

Analysis

	Cu	Br	S
Calculated	25.1%	31.6%	12.7%
Found	24.8%	31.3%	12.3%

Method 2. A mixture was made up composed of 128 g. (0.341 moles) of bis-(p-bromophenyl)disulfide, 38 g (0.598 moles) of freshly prepared copper dust, 1.5 l. of n-butyl alcohol, and 5 ml of pyridine. This was placed in a 3 l. three-necked flask fitted with a reflux condenser and stirrer. The stirred reaction mixture was heated at reflux for 5.5 days. Then the precipitate was filtered, washed with benzene, and dried for 64 hours at 80°C under vacuum. Yield was 150 g or 99.8%.

Analysis

	C	H	Br	Cu
Calculated	28.52%	2.01%	31.62%	25.14%
Found	28.36%	1.72%	31.67%	24.25%

The fresh copper dust was made as follows: To 149 g (0.299 moles) of copper sulfate pentahydrate in one liter of water was slowly added 41 g (0.314 moles) of zinc dust with stirring. After 15-20 minutes 10 ml of concentrated hydrochloric acid was added to remove any excess zinc. The mother liquor was decanted off and the residue washed with water, acetone, and then n-butyl alcohol decanting off the liquid each time. The fresh copper dust still wet with n-butyl alcohol was then added to the reaction mixture above.

Cuprous p-Chlorothiophenoxide. This monomer was prepared in 97.9% yield and greater than 95.0% purity by method 1.

Cuprous m-Bromothiophenoxide. This material was also prepared by method 1 in a 36.2% yield and greater than 95.0% purity.

Potassium p-Bromothiophenoxide. A mixture was made up of 1.00 g (0.0256 moles) of potassium metal and 4.56 g (0.0256 moles) of anthracene in 75 ml of tetrahydrofuran in the dry box. This mixture was stirred about 24 hours to form a solution of potassium-anthracene complex. The resulting complex was filtered into 5.05 g (0.0134 moles) of bis-(p-bromophenyl)disulfide in 25 ml of tetrahydrofuran and the solution so formed was stirred one hour. After filtration and after drying at less than 0.1 micron pressure for 30 hours at 125°C, a 4.07 g or 93.1% yield of potassium salt was obtained that had a 100% purity by silver nitrate titration.

1,4-Bis(ethylthio)benzene. A mixture of 236 g (1 mole) of p-dibromobenzene, 200 g of sodium ethylmercaptide, 25 g of cuprous bromide and 500 ml of 2,4-lutidine (or monoiso-propanolamine) is stirred and heated under gentle reflux for

about 30 hours. The mixture is then permitted to cool to room temperature and is then poured into ice and excess concentrated hydrochloric acid. A solid separates, is collected by filtration and then extracted with ether. The ether solution is washed once with a small portion of 5% hydrochloric acid and is dried over potassium carbonate. On evaporation of the ether a solid is obtained in a yield of 175 g or 88.2%. The compound can be recrystallized from ethanol. White leaflets, m.p. 45-46°.

1,4-Benzenedithiol. To a mixture of 50 g of 1,4-bis(ethylthio) benzene in about 500 ml of liquid ammonia is added sodium in small portions with stirring, until the blue color of the sodium solution in ammonia persisted for more than 20 minutes. Ammonium chloride (an equimolar amount to the amount of sodium used) is then added very carefully and in very small portions at first. After completed addition the ammonia is allowed to evaporate. The residue is dissolved in water, the water solution filtered and acidified with cold hydrochloric acid (1:1). The compound precipitates, is collected by filtration and recrystallized from aqueous ethanol. White leaflets, m.p. 97-98°. Yield 35.5 g or 99.0%.

Disodium Salt of 1,4-Benzenedithiol. This material was prepared by the use of the sodium-naphthalene complex technique described in WADD Technical Report 61-139. The yield was 93.0% and the purity by silver nitrate titration was 100%.

Crosslinking

Bromination of Linear Phenylene Sulfide Polymer. To 2.009 g (0.0186 mer weights) of linear phenylene sulfide polymer (M.P. 265-270°C) was added 10 ml (0.195 moles) of bromine. The reagents were allowed to stand overnight. Then the excess bromine was evaporated off. Yield was 4.99 gms (M.P. 300-310°C), a weight increase indicating the addition of about two bromine atoms per repeating unit. Elemental analysis showed it to be actually 1.67 bromine atoms per repeating unit.

The above process was repeated using 1.57 g (0.0146 mer weights) of polymer and 0.075 ml (0.00146 moles) of bromine. This resulted in the introduction of 0.096 bromine atoms per repeating unit or one in ten repeating units as shown by the weight gain and elemental analysis. Yield was 1.69 g (M.P. 267-276°C).

Crosslinking of Brominated Polymer with Sodium Sulfide. Mixtures were made up of the two brominated polymers above and sodium sulfide in pyridine such that there was one mole of sodium sulfide for every two bromine atoms in the polymers. These mixtures were heated for 48 hours at 250°C in glass

ampoules in the same manner that polymerizations were run. Conversions were 96-100%. The yields were 95-100%.

Crosslinking with Chlorosulfonic Acid. Into 0.50 g (0.0046 mer weights) of linear phenylene sulfide polymer was dropped 0.04 ml (0.00061 moles) of chlorosulfonic acid. The resulting mixture was heated at 150°C for 18 hours. Then it was diluted with water, filtered, and the residue washed with water. Yield on drying was 0.52 g which corresponds to a 55.4% yield of sulfone crosslinks.

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Aeronautical Systems Division, Wright-Patterson AF Base, Ohio. Rpt No. ASD-TDR-62-322. PHENYLENE SULFIDE POLYMERS. March 62, 52p. incl figs. and tables.

Unclassified Report

The investigation of phenylene sulfide polymers has been divided into four areas of endeavor. These are a kinetic study of a model reaction, monomer synthesis, polymerization, and determination of polymer properties. From the results of the kinetic study and monomer synthesis coupled with the early results in the other two fields cuprous p-bromothiophenoxide has been chosen as the monomer of

(over)

UNCLASSIFIED

1. Polymers
2. Kinetic study
3. Monomer synthesis
4. Polymerization

I. AFSC Project 7340 Task 734004

II. Contract AF 33 (616)-7251

III. Dow Chemical Co. Midland, Mich.

IV. H. A. Smith, C. E. Handlovits

V. Not aval fr OTS

VI. In ASTIA collection

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choice for the preparation of linear phenylene sulfide polymers. Later work on this monomer has shown that a number average degree of polymerization greater than 400 can be obtained either by solid state or solution polymerization. This polymer which has useful polymeric properties is stable in air or nitrogen to 450°C and forms a polymeric residue stable to 900°C under nitrogen.

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